The Chemistry of Dinitrogen Residues. Part 1. Diazenido-complexes of Titanium, and some Substituted Analogues. *X*-Ray Crystal Structures of $[Ti(C_5H_5)Cl_2(NNPh)]$, $[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]$, and $[Ti(C_5H_5)Cl_2(NPPh_3)]$ †

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The structures of $[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]$, $[Ti(C_5H_5)Cl_2(NPPh_3)]$, and $[Ti(C_5H_5)Cl_2(NNPh)]$ are described. The first two compounds contain $NCBu^nBu^t$ and $NPPh_3$ bound end-on with Ti–N double bonds which are rare. The last contains a unique side-on NNPh group. The NNPh can be removed from the complex as phenylhydrazine upon reaction with acid.

The protonation of dinitrogen bound to transition metals is still a rather rare and ill understood phenomenon.[1] We have attempted to elucidate the reaction routes involved, but have been able to characterise chemically and kinetically only two intermediate steps between dinitrogen and ammonia or hydrazine, namely diazenide (NNH) and hydrazide (NNH_2).[2] The breakdown of NNH_2 is far from delineated. In addition, intermediates which might arise from the protonation of bridging N_2 have yet to be defined.

We have embarked on a programme to synthesise complexes containing groups such as NNH, NNH_2, and NHNH or their organic derivatives in order to determine what their fundamental structural and reactivity properties are. For this reason, we have not concerned ourselves with the problem of deriving these from co-ordinated N_2, because this would be too restrictive; we wished to investigate a wide range of co-ordination environments which reliance on dinitrogen complexes as precursors would necessarily exclude in the current state of our knowledge. We decided to work with Ti^{IV} in the first instance, for two reasons. First, Ti^{IV} would exclude breakdown involving reduction of the dinitrogen residue by the metal, such as is believed to occur during the conversion of N_2 into NH_3 when bound to Mo or W.[3] Secondly, $[Ti(C_5H_5)Cl_3]$ has one substitution-labile chloride which facilitates simple, clean metathetical reactions, without complications of multiple metatheses.[4]

This paper discusses compounds derived from NNH and some structural analogues, $N{=}CH_2$ and $N{=}PH_3$. Derivatives related to NH_2, NHNH, and N_2H_3 will be described subsequently. A preliminary communication has already appeared.[5]

Results

(*a*) *Structures in the Solid State.*—The compound $[Ti(C_5H_5)Cl_2(NNH)]$ is not available. However, $[Ti(C_5H_5)Cl_2(NNPh)]$ has been synthesised as an orange dioxygen-stable solid by reaction of $[Ti(C_5H_5)Cl_3]$ with $Me_3SiN{=}NPh$.[6] However, although $\nu(N_2)$ is split, very weak, and low at 1 593, 1 632 cm^{-1} no convincing explanation has been suggested. We therefore performed an *X*-ray structural analysis.

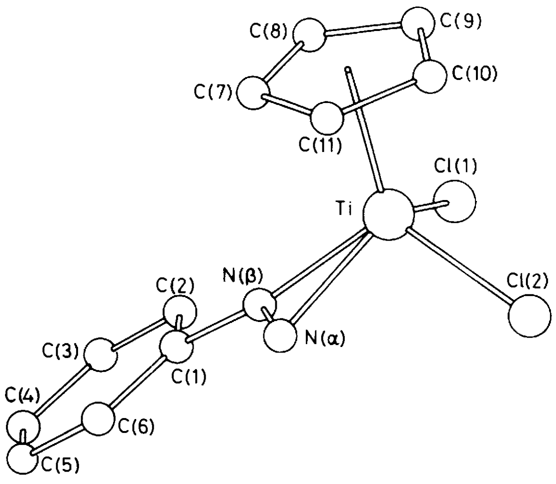
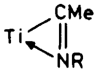


Figure 1. The molecular structure of $[Ti(C_5H_5)Cl_2(NNPh)]$

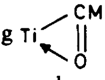
The structure is shown in Figure 1, and important bond lengths and angles are detailed in Table 1. The compound crystallises with eight molecules in the unit cell, distributed in four asymmetric pairs, each member of the pair being structurally similar though crystallographically independent. Each molecule contains the unique side-on diazenide ligand, NNPh, not yet recognised in any other structure. The TiNN system is a triangle which is almost isosceles and the Ti, nitrogens, and phenyl carbons lie in a plane. The two nitrogen and two chlorine atoms confer pseudo-C_{4v} symmetry on the titanium, which is symmetrically capped by the cyclopentadienyl group. It is interesting that *ab initio* calculations suggest just this type of side-on bonding for the hypothetical Li(NNH).[7]

There are two other types of complex in the literature which are closely allied to the current one, $[Ti(C_5H_5)_2(CMe{=}NR)]$ (R = aryl) which has been suggested[8] to contain a grouping



$\mathrm{Ti}\begin{array}{l}\diagup\,\mathrm{CMe}\\ \quad\Vert\\ \nwarrow\,\mathrm{NR}\end{array}$

and $[Ti(C_5H_5)_2Cl(MeC{=}O)]$ which has been shown to contain the grouping



$\mathrm{Ti}\begin{array}{l}\diagup\,\mathrm{CMe}\\ \quad\Vert\\ \nwarrow\,\mathrm{O}\end{array}$

by *X*-ray structure analysis.[9] Apart from these, the only comparable structures involve elements other than titanium, in $[Ni(CNBu^t)_2(NNC_{13}H_8)]$[10]

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† Dichloro(η-cyclopentadienyl)-(N^2-phenyldiazenido-N^1,N^2)titanium(IV), -(n-butyl-t-butylmethyleneamido-*N*)titanium(IV), and -(triphenylphosphoranediylamido-*N*)titanium(IV).

Supplementary data available (No. SUP 56396, 20 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected bond lengths (Å) and angles (°) for [Ti(C_5H_5)Cl_2(NNPh)]

	Molecule			Molecule	
	1	2		1	2
Ti–N(α)	2.053(5)	2.050(5)	Ti–N(α)–N(β)	70.4(3)	70.8(3)
Ti–N(β)	2.004(4)	2.012(4)	Ti–N(β)–N(α)	74.8(3)	74.2(3)
Ti–Cl(1)	2.305(2)	2.313(2)	N(α)–Ti–N(β)	34.8(2)	35.0(2)
Ti–Cl(2)	2.286(2)	2.275(2)	Ti–N(β)–C(1)	158.5(4)	159.4(5)
N(α)–N(β)	1.215(8)	1.222(8)	N(α)–N(β)–C(1)	126.7(5)	126.4(5)
N(β)–C(1)	1.439(7)	1.438(7)	Cl(1)–Ti–Cl(2)	97.1(1)	97.2(1)
Ti–C_5H_5*	2.026(6)	2.021(6)	Cl(1)–Ti–N(β)	92.6(2)	93.4(2)
Ti–C(av.)	2.348(6)	2.344(7)	Cl(2)–Ti–N(α)	90.1(2)	90.3(2)
C(1)–C(2)	1.381(9)	1.377(9)	C_5H_5*–Ti–Cl(1)	115.3(2)	116.1(2)
C(1)–C(6)	1.384(9)	1.363(9)	C_5H_5*–Ti–Cl(2)	118.8(2)	117.2(2)
C–C(cp) (av.)	1.40(1)	1.40(1)	C_5H_5*–Ti–N(α)	110.7(2)	109.3(2)
C–C(Ph) (av.)	1.380(9)	1.375(9)	C_5H_5*–Ti–N(β)	114.4(2)	115.1(2)

* Centroid of the cyclopentadienyl (C_5H_5, cp) ring.

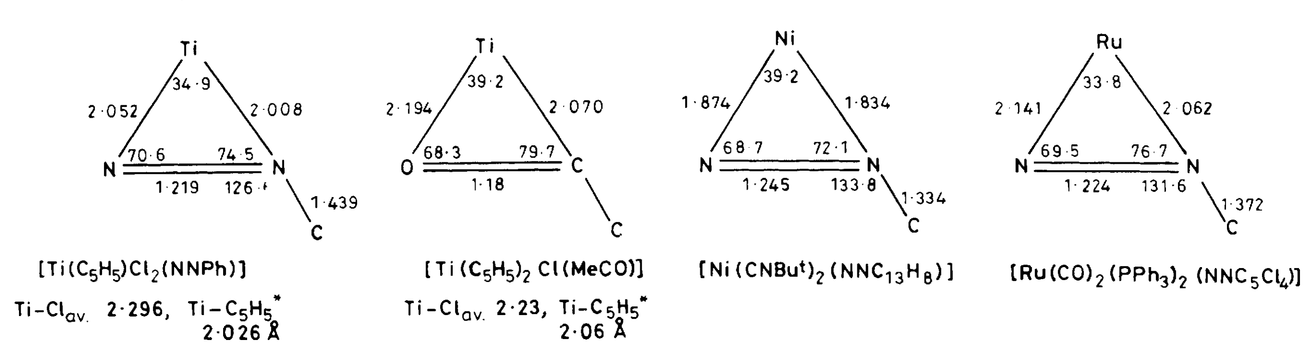
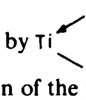
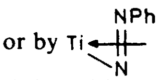


Figure 2. Detailed geometry (distances in Å, angles in °) of side-on bonding of the unsaturated groupings in [Ti(C_5H_5)Cl_2(NNPh)] and related species

($NNC_{13}H_8$ = diazofluorene) and [Ru(CO)$_2$(PPh$_3$)$_2$(NNC$_5$Cl$_4$)](NNC$_5$Cl$_4$ = tetrachlorodiazocyclopentadiene).[11] The important parts of the structures are shown in Figure 2.

The mean TiCl and TiC_5H_5 (centroid) bond lengths in the phenyldiazenido-compound are 2.296(2) and 2.026(6) Å, respectively, not very different from comparable lengths in [Ti(C_5H_5)Cl_3].[12] The N–N bond length is 1.215(8) Å, which is a plausible double-bond length. The almost equal titanium–nitrogen bonds are shorter than formal N→Ti bonds as in the 8-hydroxyquinolinato complex [Ti(C_5H_5)Cl(OC_9H_6N)$_2$] (2.247 Å),[13] but longer than the accepted Ti–N single-bond length of 1.905 Å.[14] The angles in the triangles of the compounds are very similar, that at the metal necessarily being very acute.

This structure poses several questions. (*i*) Is the anionic ligand N=NPh bonded to the titanium in a mode better described by  or by  ? (*ii*) What controls the orientation of the phenyl ring with respect to the TiNN plane? (*iii*) Is the side-on binding of N_2Ph^- a function of the anion itself or is it a configuration enforced by the metal atom and unlikely to be characteristic of other environments? (*iv*) Why is the side-on configuration preferred to the end-on bonding Ti $\underline{\leftarrow}$ N=NPh which would be equally plausible on electron-counting grounds? We can only begin to answer these questions.

The N–N bond is relatively short, compared to those in free diazene molecules (1.23 Å in MeN=NMe),[15] but end-on co-ordinated NNR (R = aryl) may exhibit considerably shorter bond lengths {*ca.* 1.14 Å in [RuCl$_3$(N$_2$C$_6$H$_4$Me-4)(PPh$_3$)$_2$]}.[16] Consequently, one might regard the N–N bond as a triple bond lengthened by π-olefinic or π-acetylenic bonding. We can use the model of Hoffmann and co-workers[17] developed for the system [Fe(C_5H_5)(CO)$_2$]$^+$ and consider the complex as being constructed formally from the moieties [Ti(C_5H_5)Cl_2]$^-$ and PhN≡N$^+$. In these circumstances there are two π interactions of the ligand with the metal which define the stereochemistry (see Figure 3). This is based on symmetry considerations only, since we have no knowledge of the orbital energies. The N–N π orbital which also overlaps with the phenyl ring interacts with metal d_{yz} orbital. There is also an overlap in the TiNN plane of the second N–N π orbital with the d_{z^2} orbital. Consequently, the bonding in these terms is best regarded as involving orbitals delocalised over both nitrogens.

The alternative description, in which we form two bonds, formally N→Ti and N–Ti, would be expected to lead to asymmetric bonding, which is not observed. In addition, groups which cannot be formulated with a triple bond, among which is N=CH$_2$ (see below), may not be genuine analogues of NNH, since they are 'isoelectronic' but not 'isolobal.' This provides some rationalisation concerning questions (*i*) and (*ii*).

Questions (*iii*) and (*iv*) are also interconnected. It has long been recognised that multiple-bond formation is restricted to certain areas of the Periodic Table. In particular, the tendency to multiple-bond formation, say to oxygen, is relatively low at the left-hand end of the First Transition Series, but rises to a

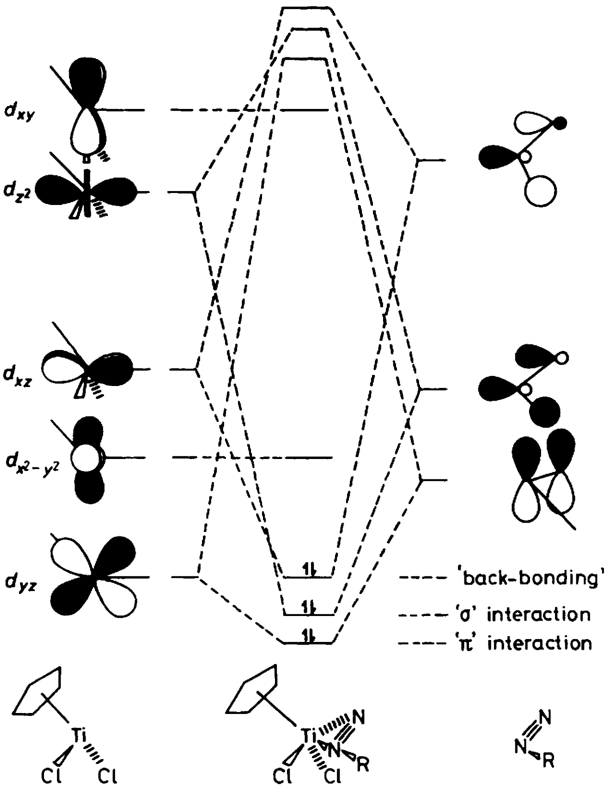


Figure 3. Significant orbital overlaps in a possible bonding scheme for $\mathrm{Ti(C_5H_5)Cl_2^-}$ to $\mathrm{NNPh^+}$

maximum at about Group 6,* thereafter falling rapidly.[18] Elements which do not easily form double bonds tend to give rise to dinuclear or polynuclear species which avoid multiple bonds but result in the same formal electron count as for the hypothetical mononuclear species (particularly true of titanium).[19] The reason for this is not clear. However, the side-on mode adopted by NNPh in this case may be due to the delocalisation of charge enforced by the low effective nuclear charge of titanium which is reflected in its low ionisation energy.[20] This would be expected to increase moving through vanadium to chromium: the chromium analogue $\mathrm{[Cr(C_5H_5)Cl_2(NNPh)]}$, if obtainable, should have the diazenide bound end-on, and probably linear. This will be tested in the near future.

In another test of these ideas, we studied further titanium compounds formally analogous to $\mathrm{[Ti(C_5H_5)Cl_2(NNPh)]}$, such as alkyldiazenido-complexes, but also some not capable of being represented by structures with triple bonds, as with $\mathrm{PhN{\equiv}N^+}$, and without lone-pair electrons on the potentially *exo*-atoms.

The compounds $\mathrm{[Ti(C_5H_5)Cl_2(N{=}CBu^nBu^t)]}$, $\mathrm{[Ti(C_5H_5)Cl_2(NPPh_3)]}$, and $\mathrm{[Ti(C_5H_5)Cl_2(NNBu^t)]}$ were also prepared. The first two were prepared by reaction of $\mathrm{[Ti(C_5H_5)Cl_3]}$ with $\mathrm{Li(NCBu^nBu^t)}$, itself obtained from $\mathrm{Bu^tCN}$ and $\mathrm{LiBu^n}$, and with $\mathrm{Me_3SiN{=}PPh_3}$. The butyldiazenido-complex was obtained by the novel reaction of $\mathrm{[Ti(C_5H_5)Cl_2(NHNHBu^t)]}$ with $\mathrm{EtO_2CNNCO_2Et}$, a route which enabled us to prepare $\mathrm{[Ti(C_5H_5)Cl_2(NNPh)]}$ from $\mathrm{[Ti(C_5H_5)Cl_2(NPhNH_2)]}$, but not $\mathrm{[Ti(C_5H_5)Cl_2(NNMe)]}$ from $\mathrm{[Ti(C_5H_5)Cl_2(NHNHMe)]}$. This reaction has the potential for the general syntheses of

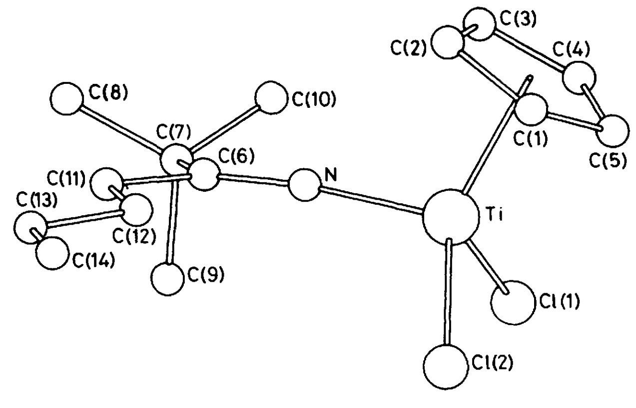


Figure 4. The molecular structure of $\mathrm{[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]}$

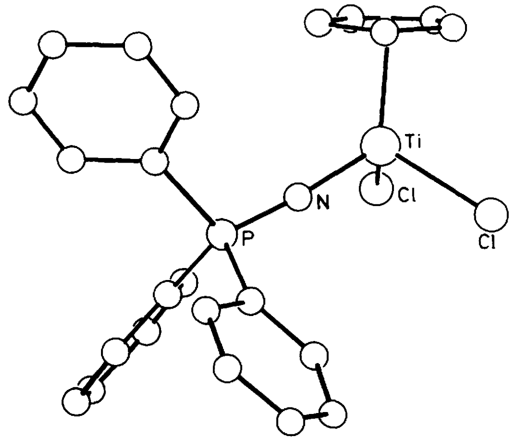
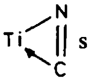


Figure 5. The molecular structure of $\mathrm{[Ti(C_5H_5)Cl_2(NPPh_3)]}$

alkyldiazenido-complexes from the more easily prepared monoalkylhydrazido(1 −)-complexes. Normally such compounds are not accessible, because the obvious reagents such as alkanediazonium salts are not available.

The structures of $\mathrm{[Ti(C_5H_5)Cl_2(N{=}CBu^nBu^t)]}$ and of $\mathrm{[Ti(C_5H_5)Cl_2(NPPh_3)]}$ are shown in Figures 4 and 5. Important bond lengths and angles are shown in Tables 2 and 3. The most significant aspect of both structures is the linear end-on bonding of the $\mathrm{NCBu^nBu^t}$ and $\mathrm{NPPh_3}$ residues. These residues can both be written as containing double bonds and could conceivably act as olefin-type ligands, but neither the C nor the P possesses a lone pair of electrons.

The ketimido-complex is monomeric. The TiCl and $\mathrm{TiC_5H_5}$ (centroid) distances are 2.280(2) and 2.024(5) Å, not very different from the values reported above for the diazenido-complex. The TiNC linkage is almost linear [171.3(4)°], but the TiN separation, at 1.872(4) Å, is very short, certainly shorter than a formal TiN single bond.[14] The NC bond length is 1.267(6) Å, a typical double bond, somewhat shorter than in $\mathrm{LiN{=}CBu^t_2}$ (1.30 Å)[21] and essentially equal to the NC bond in $\mathrm{[Zr(C_5H_5)_2(N{=}CHPh)]}$ [1.259(7) Å].[22]

The ketimido-group can act as a bridging three-electron donor as in $\mathrm{[\{Fe(CO)_3(N{=}CR_2)\}_2]}$ ($\mathrm{R = C_6H_4Me}$-4).[23] Each nitrogen atom bridges between two irons. This does not occur in our case, possibly due to the steric influence of the two butyl groups. It cannot act as a three-electron donor in the sense  since the carbon carries no lone pair, and if our

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* Group numbering follows current I.U.P.A.C. recommendations; this refers to the old transition-metal Group 6A.

Table 2. Selected bond lengths (Å) and angles (°) for [Ti(C_5H_5)Cl_2-(NCBu^nBu^t)]

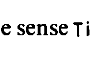
Ti-N	1.872(4)	C_5H_5*-Ti-Cl(1)	119.0(2)
Ti-Cl(1)	2.281(2)	C_5H_5*-Ti-Cl(2)	116.9(2)
Ti-Cl(2)	2.279(2)	C_5H_5*-Ti-N	109.7(2)
Ti-C_5H_5*	2.024(5)	Cl(1)-Ti-Cl(2)	100.1(1)
N-C(6)	1.267(6)	Cl(1)-Ti-N	106.1(1)
C(6)-C(7)	1.550(6)	Cl(2)-Ti-N	103.3(1)
C(6)-C(11)	1.497(7)	Ti-N(1)-C(6)	171.3(4)
Ti-C(av.)	2.338(7)	N-C(6)-C(7)	120.2(4)
C(11)-C(12)	1.508(7)	N-C(6)-C(11)	121.5(4)
C(7)-C(8)	1.514(8)	C(7)-C(6)-C(11)	118.1(4)
C-C(cp) (av.)	1.377(9)		

* Centroid of the cyclopentadienyl ring.

Table 3. Selected bond lengths (Å) and angles (°) for [Ti(C_5H_5)Cl_2-($NPPh_3$)]·0.5C_6H_5Me

Ti-N	1.78(1)	C_5H_5*-Ti-N	120.9(7)
Ti-Cl(1)	2.278(6)	C_5H_5*-Ti-Cl(1)	114.7(5)
Ti-Cl(2)	2.273(6)	C_5H_5*-Ti-Cl(2)	111.8(5)
Ti-C_5H_5*	2.04(2)	Ti-N-P	174.7(9)
N-P	1.56(1)	Cl(1)-Ti-Cl(2)	102.0(2)
P-C(av.)	1.78(2)	Cl(1)-Ti-N	102.7(5)
Ti-C(av.)	2.35(2)	Cl(2)-Ti-N	102.5(5)
C-C(Ph) (av.)	1.38(3)	N-P-C(av.)	111.7(7)
C-C(cp) (av.)	1.37(3)	C-P-C(av.)	107.1(7)

* Centroid of the cyclopentadienyl ring.

rationalisations concerning the side-on binding of diazenide are correct, then bonding in the sense  is excluded because no sensible structure can be written for the ketimide which contains a CN triple bond. Consequently, the end-on configuration here is probably enforced, and the ketimide is a three-electron donor through a highly unusual titanium–nitrogen multiple bond, *viz.* $\mathrm{Ti}\leftrightarrows\mathrm{N{=}CR_2}$ (see Figure 6). This is a conventional formulation of a metal–nitrogen multiple bond as in metal nitrosyls, for example.

The phosphiniminate is bonded end-on to the Ti(C_5H_5)Cl_2 fragment, with the TiNP skeleton almost linear [174.7(9)°]. The TiCl [2.276(6) Å] and TiC_5H_5 (centroid) [2.038(20) Å] bond lengths are very similar to those encountered in earlier structures. The C_5H_5TiClClN fragment, as in the ketimido-complex, has approximate C_{3v} symmetry. However, in this case TiN is even shorter [1.775(13) Å], though this is of no obvious significance. The NP separation in the few phosphiniminate complexes of which the structure has been determined is *ca.* 1.6 Å (comparable to the PN separation in phosphonitrilic compounds),[24] and the metal–nitrogen bond length is shorter than the sum of the single-bond covalent radii. Hence, phosphiniminate is probably a three-electron donor in all cases studied including the present one. The NP separation here, 1.563(13) Å, is consistent with a degree of double-bond character. Consequently, in this case again, the absence of a triple bond and an available lone pair enforces the end-on configuration with considerable Ti–N double-bond character. Why the compound does not form a dinuclear structure is again not clear, but the reasons are probably steric.

We also synthesised and characterised the complex [Ti(C_5H_5)Cl_2(PhNNNPh)] to discover how this three-atom nitrogen donor might bind to titanium. Unfortunately, we were unable to prepare crystals suitable for *X*-ray structure analysis.

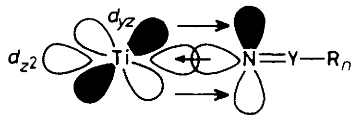


Figure 6. End-on titanium–nitrogen multiple bonding in [Ti-(C_5H_5)Cl_2(NYR_n)] (n = 2, Y = C, R = Bu^n and Bu^t; n = 3, Y = P, R = Ph)

(*b*) *Characterisation of the Complexes.*—Physical data for the complexes are presented in Table 4. All the compounds were obtained as crystalline solids, but [Ti(C_5H_5)Cl_2(NNBu^t)] was not particularly pure. However, its properties leave little doubt that it has been correctly formulated. The i.r. spectra all show typical absorptions characteristic of the C_5H_5 rings and also, where appropriate, Ph groups; ν(TiCl) and ν(TiN) were assigned by comparison with appropriate literature data.[25] However, despite the unequivocal identification of three of the compounds in the solid state, the solution ^1H n.m.r. spectra show some complications.

The two signals assigned to the methyl protons in the ^1H n.m.r. spectrum of [Ti(C_5H_5)Cl_2(NNBu^t)] are in the approximate ratio of 2:1 (1.33 p.p.m. peak:1.45 p.p.m. peak). The reason for this is not clear, but, of course, the sample was not altogether pure. The spectrum of [Ti(C_5H_5)Cl_2(NCBu^nBu^t)] is not so easily dismissed. The C_5H_5 resonance occurs as two singlets rather than one, and the Bu^t methyls similarly give rise to two singlets. There is also a broad resonance at 12.89 p.p.m., which is a region assignable to N*H*.

Independent measurements on HN=CBu^nBu^t show that this has a resonance assignable to Bu^t at 1.40 p.p.m., another assignable to Bu^n (methyl) at 1.00 p.p.m., and a broad N*H* resonance at 12.89 p.p.m. Consequently, the observed spectrum of the sample of [Ti(C_5H_5)Cl_2(NCBu^nBu^t)] is probably due to the compound itself, plus hydrolysis product. The two C_5H_5 resonances would also be consequent upon this hydrolysis.

(*c*) *Reactions.*—All the complexes are stable to dioxygen though very reactive with moisture. Their chemistry has not been investigated, with the notable exception of the protonation and alkylation of [Ti(C_5H_5)Cl_2(NNPh)].

The ligand NNPh, usually bound end-on and singly bent, is known, when it is reactive, to undergo alkylation and protonation to yield hydrazido(2−)-derivatives. Since [Ti-(C_5H_5)Cl_2(NNPh)] is the first example of side-on co-ordination, it was clearly of interest to investigate such reactivity.

Reaction of [Ti(C_5H_5)Cl_2(NNPh)] with 1 mole equivalent of HCl or HBF_4 yields a solid adduct formulated as [Ti-(C_5H_5)Cl_2(N_2HPh)]X (X = Cl or BF_4). It could not be obtained analytically pure and it decomposed upon attempted recrystallisation. Reaction of the complex with 10 mole equivalents of anhydrous hydrogen chloride in acetonitrile or tetrahydrofuran produced a white precipitate of [PhNHNH_3]Cl, in about 40% yield. The phenylhydrazine hydrochloride was identified by analysis and spectroscopy. Other products include benzene (detected by gas chromatography and ^1H n.m.r. spectroscopy) and N_2 (determined by mass spectrometry).

The course of this reaction is obscure. The production of hydrazine from diazene and the limited yield (under 50% phenylhydrazine) suggest that a redox disproportionation has occurred, but it is not clear what has been oxidised, and the products offer no clue as to the mechanism. The more usual diazenido-complexes which protonate do so to give hydrazido(2−)-complexes, but protonate no further.[1] In special cases, it is possible to convert diazenido-complexes into

Table 4. Characterisation of titanium diazenido-complexes and some analogues

		Analysis[a] (%)					
Complex	Colour	C	H	N		I.r. spectra[b] (cm^{-1})	^1H N.m.r. spectra[b] (p.p.m.)
$[Ti(C_5H_5)Cl_2(NNPh)]$[c]	Red	45.1 (45.8)	3.5 (3.5)	9.7 (9.3)	ν(NN) ν(CN) ν(TiN) ν(TiCl)	1 550w 1 260w 535s 390s	7.8 (m, 6, Ph), 6.5 (s, 5, C_5H_5)
$[Ti(C_5H_5)Cl_2(NNBu^t)]$	Brown	37.0 (40.2)	5.5 (5.2)	10.0 (10.5)	ν(NN) ν(TiN) ν(TiCl)	1 595m 530w, 550w 390w	6.65 (br s, 5, C_5H_5), 1.45 (s), 1.33 (s) (total 9, CH_3)
$[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]$	Red	52.5 (52.0)	4.6 (5.3)	7.3 (7.1)	ν(CN) ν(TiN) ν(TiCl)	1 640, 1 650br, s 560s 395s	6.66 (s), 6.63 (s) (total 5, C_5H_5), 1.80 (m, 6, CH_2), 1.40 (s), 1.20 (s) [total 9, $C(CH_3)_3$], 0.99 (t, 3, CH_2CH_3)
$[Ti(C_5H_5)Cl_2(NPPh_3)]\cdot 0.5C_6H_5Me$[d]	Yellow	62.3 (62.8)	2.7 (2.7)	4.8 (4.7)	ν(PN) ν(TiN) ν(TiCl)	1 120, 1 140s 540s 490s	7.75 (m, 17, Ph), 6.41 (s, 5, C_5H_5), 2.40 (s, 1.5, $C_6H_5CH_3$)
$[Ti(C_5H_5)Cl_2(PhNNNPh)]$	Green-black	53.9 (53.8)	4.4 (4.0)	10.7 (11.1)	ν(CN)	1 290, 1 270	*ca.* 7.1 (vbr m)

[a] Calculated values in parentheses. [b] s = Strong (i.r.) or singlet (n.m.r.), m = medium (i.r.) or multiplet (n.m.r.), w = weak, br = broad, and t = triplet; n.m.r. relative intensities are given in parentheses; solvents generally CD_2Cl_2 for n.m.r., Nujol mulls for i.r. [c] $\lambda_{max.}$ = 372 nm (ε = 7 468 l mol^{-1} cm^{-1}). [d] $\lambda_{max.}$ = 380 nm (ε = 8 515 l mol^{-1} cm^{-1}).

hydrazide(1−) derivatives but such conversions involve successive attack by nucleophiles and electrophiles. For example, $[Re(C_5H_5)(CO)_2(NNR)]^+$ (R = C_6H_4Me-4) reacts with methyl-lithium to produce $[Re(C_5H_5)(CO)_2(NNMeR)]$, which can protonate to yield the hydrazido(1−)-complex $[Re(C_5H_5)(CO)_2(NHNMeR)]^+$.[26] Clearly, no such options are available to the titanium diazenido-complex. The reaction is acid-dependent, because an excess of HBF_4 gives bright red solutions but no phenylhydrazine was detected. The salt $[OMe_3][BF_4]$ produces an intractable red oil.

Nucleophiles such as $LiBu^n$ and NaH do not react with $[Ti(C_5H_5)Cl_2(NNPh)]$ and gave only starting material upon work-up. Thallium tetrafluoroborate in acetonitrile abstracts a chloride to yield what appears to be $[Ti(C_5H_5)Cl(NNPh)(MeCN)_n]$ ($0 < n < 1$), whereas the starting complex itself does not react with bases such as MeCN. However, attempts to displace the MeCN by further nucleophiles failed. We conclude that side-on NNPh is relatively firmly bound to titanium and is unreactive, and its characteristic reactivity pattern remains to be evaluated.

Experimental

Structure Determinations.—$[Ti(C_5H_5)Cl_2(NNPh)]$. The compound was prepared as described in the literature.[6] Crystals were grown from a solution in diethyl ether at ambient temperature and sealed in Lindemann capillaries.

Crystal data. $C_{11}H_{10}Cl_2N_2Ti$, *M* = 289.02, monoclinic, *a* = 13.73(1), *b* = 12.85(5), *c* = 14.567(7) Å, β = 109.85(5)°, *U* = 2 419 $Å^3$, space group $P2_1/c$, *Z* = 8, D_c = 1.59 g cm^{-3}, μ(Mo-K_α) = 11.4 cm^{-1}, $\bar{\lambda}$(Mo-K_α) = 0.710 69 Å.

Data collection and processing. Syntex P3 diffractometer, ω—2θ mode, ω scan width 1.0°, ω scan speed 2.0—29.30° min^{-1}, Mo-K_α radiation, graphite monochromator. 2 592 Reflections measured ($2 < 2\theta < 42°$ at −35 °C), no absorption correction, 2 058 with $I > 2\sigma(I_o)$ used, *F*(000) = 1 168.

Structure analysis and refinement. Direct methods using SHELXTL program using the automatic direct methods routine EEES. Final *R* and *R'* values are 0.0443 and 0.0440; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o) + 0.0078\,F_o^2]$. The atomic co-ordinates are in Table 5.

$[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]$. The compound was prepared as described below. Dark red crystals were obtained from a solution of the compound in hexane and sealed in Lindemann capillaries.

Crystal data. $C_{14}H_{23}Cl_2NTi$, *M* = 323.9, monoclinic, *a* = 7.979(6), *b* = 17.86(1), *c* = 12.24(1) Å, β = 107.69(6)°, *U* = 1 661 $Å^3$, space group $P2_1/c$, *Z* = 4, D_c = 1.30 g cm^{-3}, μ(Mo-K_α) = 8.4 cm^{-1}.

Data collection. As above except that ω scan speed 2.3—29.3° min^{-1}. 2 043 Reflections measured ($2 < 2\theta < 42°$ at −35 °C), no absorption correction, 1 515 with $I > 2\sigma(I_o)$, *F*(000) = 680.

Structure analysis and refinement. Direct methods using SHELXTL program as above, all hydrogen atoms located but not refined, *R* and *R'* = 0.0423 and 0.0438, respectively. The atomic co-ordinates are in Table 5.

$[Ti(C_5H_5)Cl_2(NPPh_3)]\cdot 0.5C_6H_5Me$. This was prepared as described below. Large yellow prisms were deposited from the toluene mother-liquor, and were placed in Lindemann capillaries.

Crystal data. $C_{26.5}H_{24}Cl_2NPTi$, *M* = 505.9, monoclinic, *a* = 9.91(1), *b* = 14.13(2), *c* = 17.17(2) Å, β = 91.20(9)°, *U* = 2 404 $Å^3$, space group $P2_1/c$, *Z* = 4, D_c = 1.40 g cm^{-3}, μ(Mo-K_α) = 6.7 cm^{-1}.

Data collection. As for $[Ti(C_5H_5)Cl_2(NNPh)]$. 2 648 Reflections measured ($2 < 2\theta < 43°$ at −50 °C), no absorption correction, 2 033 with $I > 2\sigma(I_o)$ used, *F*(000) = 1 044.

Structure analysis and refinement. Direct methods using SHELXTL program as above, with all hydrogens inserted at ideal positions during final cycles of refinement. There is a disordered molecule of toluene associated with every two molecules of complex. This prevented the reliability factors being reduced below *R* = 0.12 and *R'* = 0.14. The atomic co-ordinates are given in Table 5.

The compounds $[Ti(C_5H_5)Cl_2(NNPh)]$,[6] $Me_3SiNPPh_3$,[6] $[Ti(C_5H_5)Cl_2(NHNHBu^t)]$,[27] $[Ti(C_5H_5)Cl_2(NPhNH_2)]$,[27] $Me_3SiNNPh$,[28] $[Ti(C_5H_5)Cl_3]$,[4] and $Li(NCBu^nBu^t)$[21] were synthesised by published methods. Other compounds were obtained commercially.

All operations were carried out under dry nitrogen using standard Schlenk-tube or glove-box techniques. All solvents were distilled from drying agents prior to use. U.v.–visible spectra were obtained with a Pye-Unicam SP1800 spectro-

Table 5. Final co-ordinates (fractional 10^4) for the refined atoms, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Ti(C_5H_5)Cl_2(NNPh)]$							
Ti(1)	4 976.9(8)	5 377.8(8)	7 197.3(7)	Ti(2)	140.5(8)	6 835.5(8)	2 872.1(7)
Cl(1)	4 624(1)	4 568(1)	8 461(1)	Cl(3)	673(1)	7 536(1)	1 659(1)
Cl(2)	5 671(1)	3 966(1)	6 690(1)	Cl(4)	−458(1)	8 335(1)	3 317(1)
N(1)	6 324(4)	6 191(4)	7 419(3)	N(3)	−1 278(4)	6 152(4)	2 605(4)
N(2)	6 027(3)	6 324(4)	8 106(3)	N(4)	−967(3)	5 958(3)	1 931(3)
C(1)	6 538(4)	6 921(4)	8 972(4)	C(21)	−1 494(4)	5 349(4)	1 079(4)
C(2)	7 373(5)	7 545(5)	9 022(4)	C(22)	−2 333(5)	4 752(5)	1 060(4)
C(3)	7 850(5)	8 074(5)	9 875(5)	C(23)	−2 821(5)	4 186(5)	221(5)
C(4)	7 498(5)	7 988(5)	10 655(5)	C(24)	−2 478(5)	4 217(5)	−558(4)
C(5)	6 666(5)	7 372(5)	10 589(5)	C(25)	−1 646(5)	4 828(5)	−515(5)
C(6)	6 157(5)	6 821(5)	9 734(4)	C(26)	−1 136(4)	5 401(5)	314(4)
C(7)	4 154(5)	6 943(5)	6 480(4)	C(27)	1 872(5)	6 587(5)	3 837(5)
C(8)	3 493(5)	6 433(5)	6 858(5)	C(28)	1 318(5)	6 760(5)	4 460(5)
C(9)	3 193(5)	5 495(5)	6 357(5)	C(29)	633(5)	5 944(5)	4 356(5)
C(10)	3 684(5)	5 419(5)	5 674(5)	C(30)	760(5)	5 240(6)	3 656(5)
C(11)	4 292(5)	6 316(5)	5 737(5)	C(31)	1 525(5)	5 642(5)	3 341(5)
(*b*) $[Ti(C_5H_5)Cl_2(NCBu^nBu^t)]$							
Ti	−2 917(1)	1 648.4(5)	−9 568.6(7)	C(6)	−3 795(6)	3 295(3)	−10 278(4)
C(1)	−926(9)	1 663(3)	−10 648(6)	C(7)	−5 687(6)	3 470(3)	−11 051(4)
C(2)	−2 535(8)	1 444(4)	−11 370(5)	C(8)	−5 764(8)	4 200(3)	−11 693(5)
C(3)	−2 999(8)	787(4)	−11 010(6)	C(9)	−6 809(7)	3 535(4)	−10 232(5)
C(4)	−1 714(9)	560(3)	−10 052(5)	C(10)	−6 356(7)	2 835(3)	−11 897(5)
C(5)	−380(7)	1 106(4)	−9 815(5)	C(11)	−2 611(7)	3 940(3)	−9 781(5)
Cl(1)	−1 578(2)	1 678.4(8)	−7 636(1)	C(12)	−855(7)	3 749(3)	−8 932(4)
Cl(2)	−5 632(2)	1 224.8(8)	−9 614(1)	C(13)	154(8)	4 453(3)	−8 411(5)
N	−3 320(5)	2 624(2)	−10 024(3)	C(14)	1 907(8)	4 304(3)	−7 580(5)
(*c*) $[Ti(C_5H_5)Cl_2(NPPh_3)]\cdot 0.5C_6H_5Me$							
Ti	7 444(3)	9 974(2)	3 729(2)	C(22)	3 973(16)	8 914(11)	1 240(9)
Cl(1)	7 632(7)	8 675(3)	4 510(3)	C(23)	4 342(18)	8 644(13)	456(10)
Cl(2)	9 101(4)	9 717(4)	2 858(3)	C(24)	5 565(18)	8 806(13)	194(10)
C(1)	7 971(21)	10 877(15)	4 852(11)	C(25)	6 589(17)	9 221(13)	677(10)
C(2)	8 911(22)	11 146(16)	4 345(12)	C(26)	6 292(16)	9 488(12)	1 409(9)
C(3)	8 105(21)	11 549(15)	3 769(12)	C(31)	3 654(14)	8 649(10)	3 041(8)
C(4)	6 785(21)	11 533(16)	3 890(12)	C(32)	2 238(15)	8 659(11)	3 060(8)
C(5)	6 664(22)	11 068(16)	4 596(12)	C(33)	1 576(17)	7 878(13)	3 276(10)
P	4 615(4)	9 615(3)	2 686(2)	C(34)	2 236(16)	7 045(12)	3 458(9)
N	5 958(12)	9 731(9)	3 170(8)	C(35)	3 603(17)	7 034(12)	3 428(9)
C(11)	3 572(14)	10 638(10)	2 702(8)	C(36)	4 348(17)	7 817(12)	3 202(9)
C(12)	3 015(16)	11 058(11)	2 042(9)				
C(13)	2 268(18)	11 863(13)	2 074(10)	C(1x)*	−123(43)	6 264(29)	4 893(23)
C(14)	1 989(18)	12 265(13)	2 764(10)	C(2x)	−282(21)	5 416(16)	4 407(12)
C(15)	2 556(18)	11 846(13)	3 460(10)	C(3x)	−134(32)	4 574(23)	4 806(17)
C(16)	3 270(18)	11 030(13)	3 409(10)	C(4x)	−265(26)	3 700(19)	4 407(14)
C(21)	4 941(15)	9 319(11)	1 697(8)	C(5x)	−449(46)	4 557(35)	4 021(26)

* Toluene solvent molecules disordered about the inversion centre at 0, $\frac{1}{2}$, $\frac{1}{2}$; C(1x), C(3x), and C(5x) have occupancies of 0.5.

photometer, i.r. spectra using Pye-Unicam SP2000 and SP3-200 instruments, and n.m.r. spectra using a JEOL FX 90Q machine. Analyses were by Mr. C. J. Macdonald, Unit of Nitrogen Fixation.

Dichloro(η^5-*cyclopentadienyl*)(N^2-*t-butyldiazenido*)-*titanium*.—The yellow complex $[Ti(C_5H_5)Cl_2(NHNHBu^t)]$ (0.5 g, 1.8 mmol) was dissolved in diethyl ether (25 cm^3) and diethyl azodicarboxylate (0.3 g, 1.8 mmol) was added. The colour of the solution gradually turned dark brown on stirring at room temperature overnight. The resultant brown solid was filtered off and dissolved in dichloromethane (30 cm^3). Storage of the solution at −30 °C yielded a white solid, $EtO_2CNHNHCO_2Et$, which was filtered off. The filtrate, reduced to dryness at 10^{-3} mmHg (*ca.* 0.133 Pa), gave a *solid* which was washed with hexane and dried *in vacuo*. Yield 0.15 g, 40%.

(*n-Butyl-t-butylmethyleneamido*-N)*dichloro*(η^5-*cyclopentadienyl*)*titanium*.—The salt $Li(NCBu^nBu^t)$ (0.33 g, 2.3 mmol) was added to a solution of $[Ti(C_5H_5)Cl_3]$ (0.5 g, 2.3 mmol) in dichloromethane (25 cm^3). The solution immediately turned dark red but was stirred at room temperature for 4 h. The dichloromethane was removed *in vacuo* and the residue extracted with hexane (30 cm^3). On standing at room temperature, this solution yielded dark red *crystals*. Yield *ca.* 75%.

Dichloro(η^5-*cyclopentadienyl*)(*triphenylphosphiniminato*)-*titanium–Toluene* (2/1).—The complex $[Ti(C_5H_5)Cl_3]$ (0.40 g, 1.8 mmol) and $Me_3SiNPPh_3$ (0.63 g, 1.8 mmol) were stirred together in toluene (30 cm^3) for 1 h at room temperature. The product crystallised from the reaction mixture as large yellow prisms. Yield 0.70 g, 85%. M.p. 172 °C, lit.,[6] not recorded.

Dichloro(η^5-*cyclopentadienyl*)(1,3-*diphenyltriazenido*)-*titanium*.—Reactions of PhNNNHPh (0.15 g, 0.76 mmol) and $LiBu^n$ (0.76 mmol in hexane) in diethyl ether produced dark green Li(PhNNNPh). To this solution, $[Ti(C_5H_5)Cl_3]$ (0.17 g, 0.76 mmol) in diethyl ether (20 cm^3) was quickly added, and the green solution stirred at room temperature for 15 h. A white precipitate was filtered off, and the filtrate stored at − 15 °C for 72 h. The resulting green-black crystals were filtered off and dried *in vacuo*. Yield 0.17 g, 60%. M.p. 116—118 °C.

Reactions of $[Ti(C_5H_5)Cl_2(NNPh)]$.—(*a*) *With* 1 mol *of* HCl. The complex (0.3 g, 1.2 mmol) was dissolved in dichloromethane (20 cm^3) and anhydrous HCl solution [from $SiMe_3Cl$ (0.15 cm^3, 1.2 mmol) and EtOH (0.08 cm^3, 1.2 mmol) in dichloromethane (5 cm^3)] added *via* a syringe. The red solution was stirred at room temperature for 3 h, and the solvent then removed *in vacuo*. The resultant magenta solid was washed with pentane (15 cm^3) and dried *in vacuo* {Found: C, 42.9; H, 4.6; N, 7.9. $[Ti(C_5H_5)Cl_2(NNPh)]\cdot HCl$ requires C, 40.7; H, 3.4; N, 8.6%}. The product is unstable and decomposes upon attempted recrystallisation from tetrahydrofuran or dichloromethane.

(*b*) *With an excess of* HCl. The complex (0.5 g, 2.3 mmol) in acetonitrile (20 cm^3) reacted with a ten-fold excess of HCl [generated from $SiMe_3Cl$ (3.0 cm^3, 23 mmol) and EtOH (1.4 cm^3, 22 mmol) in acetonitrile (5 cm^3)] to give a white precipitate and an orange-red solution. After stirring for 2 h at room temperature, the solid was filtered off, washed with acetonitrile (20 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo*. Yield 0.14 g, 42% (Found: C, 50.3; H, 6.0; N, 18.3. $PhNHNH_2\cdot HCl$ requires C, 49.8; H, 6.2; N, 19.3%). Dinitrogen (identified by mass spectroscopy) and benzene (identified after gas chromatography and ^1H n.m.r. spectroscopy) were also produced, though not in reproducible quantities. The metal-containing product was not identified.

(*c*) *With* $TlBF_4$. The complex (0.5 g, 2.3 mmol) and $TlBF_4$ (0.67 g, 2.3 mmol) were suspended in acetonitrile (30 cm^3) and stirred at room temperature for 96 h. The red solution gradually turned brown and deposited a fine white precipitate. This was filtered off, and the filtrate reduced to an oil *in vacuo*. Trituration of the brown oil with dichloromethane and hexane produced a dark brown solid {Found: C, 40.4; H, 3.3; N, 7.6. $[Ti(C_5H_5)Cl(MeCN)(NNPh)]BF_4$ requires C, 38.2; H, 3.4; N, 10.9. $[Ti(C_5H_5)Cl(NNPh)]BF_4$ requires C, 35.1; H, 2.9; N, 8.2%}. The Nujol-mull i.r. spectrum showed bands assignable to ν(CN) at 2 310 and $\nu(BF_4)$ at 1 070 cm^{-1}. Reactions of this product with NaH and $LiBu^n$ gave no isolable product.

(*d*) *Miscellaneous*. Reactions of $[Ti(C_5H_5)Cl_2(NNPh)]$ with HBF_4, $[OMe_3][BF_4]$, and NaH gave no isolable products.

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